

$\alpha = 106.15 (6)^\circ$   
 $\beta = 92.75 (6)^\circ$   
 $\gamma = 106.74 (6)^\circ$   
 $V = 760.2 (10) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.364 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Block  
 $0.46 \times 0.25 \times 0.20 \text{ mm}$   
 Colourless

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1147). Services for accessing these data are described at the back of the journal.

#### Data collection

Siemens P3R3 diffractometer  $\theta_{\max} = 25.05^\circ$   
 $\omega$ - $2\theta$  scans  $h = 0 \rightarrow 9$   
 Absorption correction: none  $k = -10 \rightarrow 10$   
 2905 measured reflections  $l = -13 \rightarrow 13$   
 2694 independent reflections 3 standard reflections  
 1926 reflections with every 200 reflections  
 $I > 2\sigma(I)$  intensity decay: none  
 $R_{\text{int}} = 0.023$

#### Refinement

Refinement on  $F^2$   $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   $\Delta\rho_{\min} = -0.18 \text{ e \AA}^{-3}$   
 $wR(F^2) = 0.124$  Extinction correction:  
 $S = 1.043$  SHELXL96 (Sheldrick,  
 2694 reflections 1996)  
 211 parameters Extinction coefficient:  
 H atoms not refined 0.089 (7)  
 $w = 1/[\sigma^2(F_o^2) + (0.0599P)^2$  Scattering factors from  
 $+ 0.1752P]$  International Tables for  
 where  $P = (F_o^2 + 2F_c^2)/3$  Crystallography (Vol. C)  
 $(\Delta/\sigma)_{\max} = 0.010$

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C7	1.196 (3)	O4—C17	1.345 (3)
O2—C15	1.358 (3)	O4—C4	1.388 (3)
O2—C2	1.387 (3)	O5—C17	1.189 (3)
O3—C15	1.188 (3)		
C15—O2—C2—C3	106.3 (2)	C2—C1—C7—O1	28.9 (3)
C15—O2—C2—C1	-81.5 (2)	O1—C7—C8—C9	-15.0 (3)
C17—O4—C4—C3	-60.3 (3)	C1—C7—C8—C9	163.98 (19)

The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: P3/PC Diffractometer Program (Siemens, 1989). Cell refinement: P3/PC Diffractometer Program. Data reduction: SHELXTL-Plus (Sheldrick, 1991). Program(s) used to solve structure: SHELXTL-Plus. Program(s) used to refine structure: SHELXL96 (Sheldrick, 1996). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXL96.

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### Dimethyl 9,10-Dihydro-9,10-ethenoanthracene-11-carboxylate-12-S-carbonothioate

RAY JONES, A. GRAHAM M. RATTRAY, JOHN R. SCHEFFER AND JAMES TROTTER

*Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. E-mail: jtrt@xray4.chem.ubc.ca*

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#### Abstract

The title molecule, C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>S, contains a dibenzo-barrelene skeleton, with normal geometry and dimensions. The carbomethoxy substituent is almost fully conjugated with the C11=C12 double bond [O=C—C=C torsion angle 171.3 (2)° and cos<sup>2</sup>(angle) 0.98].

#### Comment

Previous crystal structure studies of 11,12-derivatives of dibenzobarrelene have given detailed information

† Alternative name: methyl 9,10-dihydro-12-methoxycarbonylthio-9,10-ethenoanthracene-11-carboxylate.

on the structural aspects of the pathways in solid-state photochemical reactions of this class of compound (Garcia-Garibay, Scheffer, Trotter & Wireko, 1990*a,b*; Pokkuluri, Scheffer & Trotter, 1993*a,b*). The reactions proceed *via* the di- $\pi$ -methane rearrangement (Zimmerman, 1991), following one of four pathways, to give two possible dibenzosemibullvalene photoproducts (and their enantiomers). The first step in these reactions involves bond formation between vinyl (*e.g.* C12 in Fig. 1) and benzo (*e.g.* C4a) C atoms, and one of the factors influencing the pathway is the electronic effect of the substituent groups at the 11 and 12 positions. In diester derivatives, for example, one of the ester groups is usually conjugated with the C11=C12 bond, and the other non-conjugated (intramolecular steric effects prevent both being conjugated). Initial vinyl-benzo bond formation is expected to occur at the site of the less-conjugated substituent (*e.g.* at C12), as the odd electron (at C11) in the resulting biradical can then be delocalized over the conjugated ester group.

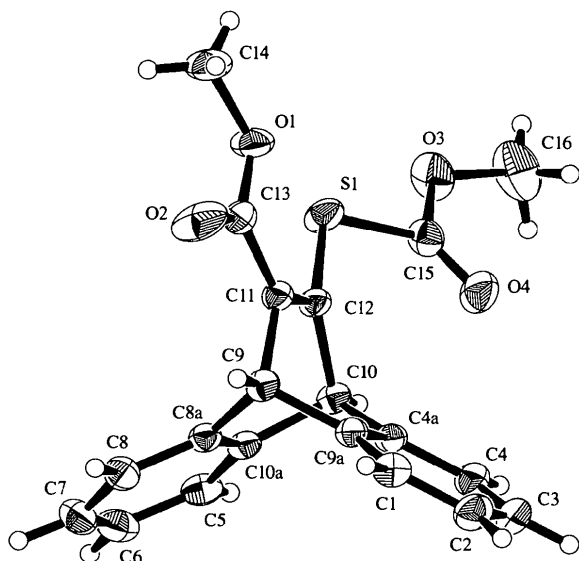
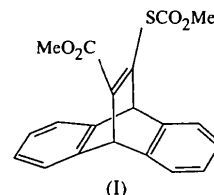


Fig. 1. View of the title molecule (33% probability ellipsoids).

Investigation of the effects on the photoreactions of varying the nature of the 11,12-substituents has been pursued by studies of amides (Jones, Rattray, Scheffer & Trotter, 1996) and of thiono and thiolesters (Jones, Rattray, Scheffer & Trotter, 1995). Synthesis of the latter two classes of compound proved to be difficult, but the thionoester was eventually obtained by treatment of a dicarboxylate with Lawesson reagent (Pedersen & Lawesson, 1979), and the thiolester by reaction of the acyl chloride of an ester-acid with methanethiol (Jones *et al.*, 1995). During these attempted syntheses, a small amount of a compound of unknown structure was obtained. The present crystal structure analysis shows this compound to be an *S*-carbonothioate, (I).



The molecule (Fig. 1) contains a normal dibenzobarrelene (9,10-dihydro-9,10-ethenoanthracene) skeleton. The carbomethoxy substituent at C11 is almost fully conjugated with the C11=C12 double bond [O2—C13—C11—C12 171.3 (2)° and  $\cos^2(\text{angle})$  0.98 (a measure of the amount of conjugation)]. The synthesis has inserted an S atom between C12 and the second carbomethoxy substituent, with  $C_{sp^2}$ —S 1.754 (2) and 1.767 (2) Å, and C—S—C 103.11 (8)°. Electronic considerations would therefore predict that photochemical reaction should proceed with initial bond formation at C12, allowing delocalization of a biradical electron over the conjugated carbomethoxy group at C11. However, no previous compounds with 11,12-bonded S have been studied, and the amount of material available was insufficient to allow a detailed photochemical study. Intermolecular contacts correspond to normal van der Waals interactions.

## Experimental

The material was obtained during the attempted synthesis of thiono- and thiolcarboxylate derivatives of dibenzobarrelene (Jones *et al.*, 1995).

### Crystal data

$C_{20}H_{16}O_4S$   
 $M_r = 352.40$   
 Monoclinic  
 $P2_1/a$   
 $a = 12.023 (2) \text{ \AA}$   
 $b = 9.446 (2) \text{ \AA}$   
 $c = 15.205 (2) \text{ \AA}$   
 $V = 1726.7 (5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.355 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.7107 \text{ \AA}$   
 Cell parameters from 21 reflections  
 $\theta = 21.7\text{--}25.1^\circ$   
 $\mu = 0.21 \text{ mm}^{-1}$   
 $T = 294 \text{ K}$   
 Prism  
 $0.50 \times 0.50 \times 0.40 \text{ mm}$   
 Colourless

### Data collection

Rigaku AFC-6S diffractometer  
 $\omega$ -2 $\theta$  scan  
 Absorption correction:  
 $\psi$  scans (North, Phillips & Mathews, 1968)  
 $T_{\min} = 0.866$ ,  $T_{\max} = 0.919$   
 5550 measured reflections  
 5322 independent reflections

3061 reflections with  $I > 3\sigma(I)$   
 $R_{\text{int}} = 0.013$   
 $\theta_{\max} = 29.99^\circ$   
 $h = 0 \rightarrow 16$   
 $k = 0 \rightarrow 13$   
 $l = -21 \rightarrow 21$   
 3 standard reflections every 200 reflections  
 intensity decay: 0.88%

## Refinement

Refinement on  $F$  $R = 0.0393$  $wR = 0.0496$  $S = 1.83$ 

3061 reflections

290 parameters

All H atoms refined

 $w = 1/[\sigma^2(F_o)$   
 $+ 0.00029|F_o|^2]$  $(\Delta/\sigma)_{\max} = 0.004$  $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$ 

Extinction correction: none

Scattering factors from

*International Tables for*  
*Crystallography* (Vol. C)Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—C12	1.754 (2)	O3—C15	1.335 (2)
S1—C15	1.767 (2)	O3—C16	1.454 (3)
O1—C13	1.326 (2)	O4—C15	1.185 (2)
O1—C14	1.448 (2)	C11—C12	1.342 (2)
O2—C13	1.199 (2)		
C12—S1—C15	103.11 (8)	C15—O3—C16	116.6 (2)
C13—O1—C14	116.9 (2)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1284). Services for accessing these data are described at the back of the journal.

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